Industrial & Engineering Chemistry Research, vol. 38, pp. 5034-5037, December 1999.

Effects of Photochemical Formation of Mercuric Oxide

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The photochemistry of elemental mercury and oxygen was examined using quartz flow reactors. Germicidal bulbs were used as the source of 253.7 nm ultraviolet radiation. The formation of mercuric oxide, as visually detected by yellow-brown stains on the quartz walls, was confirmed by both ICP-AES and SEM-EDX analyses. In addition, a high surface area calcium silicate sorbent was used to capture the mercuric oxide in one of the experiments. The implications of mercuric oxide formation with respect to analysis of gases for mercury content, atmospheric reactions, and direct ultraviolet irradiation of flue gas for mercury sequestration are discussed.

Introduction

The thermal oxidation of elemental mercury in air proceeds within the narrow temperature band

between 350 - 500°C.[1] However, ultraviolet light allows the oxidation to occur at much lower temperatures due to the formation of ozone. Mercury is a known photosensitizer for the formation of ozone from oxygen. Ozone is a powerful oxidizer that can rapidly react with elemental mercury to form mercuric oxide.

The photochemistry of mercury has been extensively studied.[2-7] Dickinson and Sherrill[2] found that 253.7 nm irradiation of oxygen in the presence of mercury vapor produced a decrease in pressure, which they ascribed to the formation of ozone, viz:

$$3\ O_{2(gas)} \rightarrow 2\ O_{3(gas)} \qquad (1)$$

Dickinson and Sherrill also noted yellow-brown deposits on the walls of their quartz reactor, which they attributed to the formation of mercuric oxide via thermal oxidation of mercury by ozone, as shown below:

$$Hg_{(gas)} + O_{3(gas)} \rightarrow HgO_{(solid)} + O_{2(gas)} \qquad (2)$$

Mercury is usually detected by the absorption or emission of 253.7 nm ultraviolet radiation. The measurement of mercury will be affected by the photosensitized ozone reaction, unless precautions are implemented, e.g., using an inert carrier gas. Many of the proposed on-line detectors (continuous emissions monitors) for mercury in flue gas are based upon atomic absorption (AAS) or atomic fluorescence spectrophotometry (AFS) utilizing 253.7 nm radiation.[8] Excited mercury atoms can

revert to the ground state when colliding with a polyatomic species. Oxygen is among the most efficient quenching agents known.[9-11] Mercury excited by the absorption of 253.7 nm ultraviolet light can initiate the formation of ozone from oxygen. The ozone can then react with mercury to form mercuric oxide, which could deposit on the quartz detection cell. Furthermore, ozone is often measured by the absorption of 253.7 nm ultraviolet radiation.[7] These two factors can greatly complicate the ultraviolet determination of mercury in carrier gases containing oxygen.

Ozone chemistry can effect the fate of mercury in coal-fired utilities. Electrostatic precipitators are used in a vast majority of coal-fired utilities. The corona discharge will generate both ultraviolet radiation and ozone.[7,12-17] Ozone can potentially react with elemental mercury in flue gas to form mercuric oxide, although it most likely reacts with other flue gas components whose concentrations are orders of magnitude larger than mercury.

Additionally, mercury has an impact upon ozone chemistry in the upper levels of the atmosphere. Mercuric oxide, associated with fine particulates, has been detected recently in the tropopause and is speculated to form by oxidation of elemental mercury by ozone.[18,19] Ground level mercury concentrations in the Arctic have also been found to vary with seasonal changes in sunlight, temperature, and upper atmosphere ozone level.[20,21] Ground level mercury could also impact the level of ground level ozone, where ozone is a prime constituent of smog.[22]

Experimental

The assembly used for studying the photochemical oxidation of mercury consists of an elemental mercury permeation tube, a quartz photoreactor, and an ultraviolet lamp. The reactor scheme is shown in Figure 1. A certified Dynacal permeation tube from VICI Metronics is used as the source of elemental mercury. The permeation tube has been certified by the manufacturer to release 144 ng Hg/min at 212°F. The permeation tube is located at the bottom of a Dynacal glass U-tube, which is maintained at 212°F ± 1.6°F at all times by immersing it in a Haake D8 oil bath. A flow (30 ml/min) of gas passes over the permeation tube and is maintained at all times with a thermal conductivity mass flow controller. The output of the permeation tube and the flow rate of carrier gas yields a calculated concentration of mercury of 585 ppb. The mercury output of the tube has been verified on a regular basis via weight loss measurement and has been found to be consistent (152 ng Hg/min) with the certified release.

Two quartz photoreactors were used to study the oxidation of elemental mercury. The first photoreactor is a 20 inch long by 1/4 inch outer diameter cylindrical quartz tube. The second photoreactor is a 1-3/4 inch long by 1/2 inch wide rectangular clear flow-through quartz cuvette from Brooks Rand. Quartz, unlike glass, is sufficiently transparent towards 253.7 nm ultraviolet radiation. All of the plumbing and valves which come into contact with mercury are constructed from either stainless steel or teflon. These materials have been demonstrated to have good chemical resistance and inertness towards mercury. A Raytech LS-7 Ultraviolet lamp was used as the source of 253.7 nm light for the 20 inch quartz photoreactor. Four watt mercury germicidal bulbs (SW-6) were used as the source of 253.7 nm radiation. Similar four watt unfiltered mercury germicidal lamps

(Bulbtronics bulb G4T5) were used as the source of 253.7 nm radiation when the quartz cuvette photoreactor was used. Eighty percent of the output radiation is 253.7 nm light.[23] All of the experiments were done at ambient temperature, at near ambient pressure, and with a carrier gas flow-rate of 30 cm^3/sec and a mercury concentration of 585 ppb.

The quartz cuvette cell was part of a detector (Brooks Rand CVAFS-2 cold vapor atomic fluorescence spectrophotometer (AFS)) for determining elemental mercury. When used as a continuous on-line monitor for elemental mercury in argon, the detection limit is around 1 ppb. The AFS is a ultraviolet detector for elemental mercury; mercury atoms absorb 253.7 nm light and re-emit (fluoresce) this wavelength. A mercury bulb serves as the ultraviolet source, and a photomultiplier tube serves as the ultraviolet fluorescence detector. Any gas can be used as a carrier, although sensitivity can vary dramatically, due to quenching of the excited Hg atoms by collisions with polyatomic species. Therefore, maximum sensitivity is achieved with high purity argon or helium carrier gases. In comparison to argon, nitrogen was found to reduce the relative response of the AFS to elemental mercury by a factor of 10. In comparison to argon, air was found to reduce the relative response of the AFS to elemental mercury by a factor of 100. This is in good agreement with the data provided by the manufacturer of the detector.[23] However, the response of the detector decayed rapidly in oxygen containing carrier gases, due to the deposition of mercuric oxide upon the quartz cell walls.

Key process parameters were recorded with a data acquisition system. This on-line data acquisition system was used to take and store the various voltage signals from the thermocouples, flowmeters,

and the atomic fluorescence spectrophotometer. Data sampling occurred every 15 seconds.

Scanning electron microscopy with energy-dispersive x-ray methods (SEM-EDX) was used to confirm the formation of mercuric oxide (HgO) on the walls of the quartz photoreactor. A Leica 360i scanning electron microscope was used with a Kevex Delta EDX spectrometer. The Kevex spectrometer is equipped with a Quantum Superdry light element detector. Inductively coupled argon plasma atomic emission spectroscopy (ICP-AES) was used to quantitatively determine the mass of mercury converted to mercuric oxide. The instrument is a Perkin-Elmer Optima 3000 Radial View Spectrometer. The yellow stains on the quartz wall were extracted with warm nitric acid. A small quantity of the solution was then aspirated into the argon torch, and mercury was quantitatively determined by the intensity of the 253.7 nm emission line.

In one test, ten milligrams of a sorbent was placed in the cylindrical reactor and irradiated. The sorbent (Manville Micro-Cel) is a synthetic calcium silicate with a BET surface area given by the manufacturer as between 100 - 200 m^2/gram. The sorbent was exposed for 350 minutes to 30 ml/min of 585 ppb Hg in air while being irradiated by 253.7 nm light. The used sorbent was digested in aqua regia and the capacity was determined by ICP-AES analysis.

Results and Discussion

The results of the removal of elemental mercury in the presence of oxygen as mercuric oxide is shown in Table 1. Mercury removals are defined as the mass of mercury deposited in the reactor divided by the inlet mass of mercury. The mass of mercury within the reactor is determined by the analysis

of the mercury deposits; the inlet mass of mercury was calculated from the known rate of mercury release from the permeation tube and the total time of the test. As can be seen in Table 1, a high level of removal for the empty quartz reactors was achieved by photoxidation. The empty cuvette reactor was part of the Brooks Rand AFS. The voltage signal from the AFS decayed rapidly in oxygen containing carrier gases. For the 4% oxygen carrier gas, the voltage signal decayed by over 56% due to the mercuric oxide film that formed within the quartz cuvette. Thus the tracking of mercury concentration with the AFS could not be conducted.

It should be noted that the recovery of mercury was accomplished by extraction with warm nitric acid. This may not be the optimal recovery method, but it was improved for the sorbent experiment. It is also noted that ICP-AES is not the optimal method for the quantitative determination of mercury. Nevertheless, SEM-EDX analysis clearly confirms the formation of mercuric oxide on the quartz walls. The formation of mercuric oxide on quartz walls in similar experiments was first noted by Dickinson.[2]

The removal of mercury as mercuric oxide captured on Micro-Cel was examined at room temperature. In this experiment, 585 ppb of elemental mercury in air was exposed to 253.7 nm radiation while passing over a high surface area calcium silicate sorbent for six hours. The mass of mercury captured on the silicate was found to be 22.5 micrograms out of the 53.2 micrograms passed over the sorbent. An improved procedure was used for the extraction of mercury from the used sorbent by soaking in aqua regia. However, some of the mercury appears to have adhered upon the quartz walls as mercuric oxide, as evidenced by a reddish-brown stain.

The mechanism for the removal of mercury as mercuric oxide was deduced by Dickinson and Sherrill[2] and Bamford and Tipper[5] and is shown below:

$$Hg + 253.7 \text{ nm light} \rightarrow Hg^* \quad (3)$$

$$Hg^* + O_2 \rightarrow Hg + O_2^* \quad (4)$$

$$O_2^* + O_2 \rightarrow O_3 + O \quad (5)$$

$$Hg + O_3 \rightarrow HgO + O_2 \quad (2)$$

$$O_2 + O \rightarrow O_3 \quad (6)$$

Reaction (3) is the excitation of elemental mercury by 253.7 nm uv radiation. Reaction (4) is the quenching of the excited mercury atom by oxygen, with the formation of an excited oxygen molecule. Step (5) is the quenching of an excited oxygen molecule, with the formation of ozone and an oxygen atom. Reaction step (2) is the thermal reaction of elemental mercury and ozone, with the formation of mercuric oxide and oxygen. Reaction (6) is the combination of an oxygen molecule with a reactive oxygen atom to form ozone.

The overall reaction is the sum of reaction steps (3), (4), (5), (2), and (6):

$$Hg + 2\ O_2 + 253.7\ nm\ light \rightarrow HgO + O_3 \quad (7)$$

Biswas[14,15] found that the longer 360 nm uv light alone is ineffective at oxidizing mercury in air. The 360 nm wavelength was highly effective when used with a titanium oxide photooxidation catalyst, capturing mercury as mercuric oxide in a heterogeneous oxidation reaction.[14,15] The experiments described in the present research note involve gas phase oxidation to convert elemental mercury to mercuric oxide, with subsequent deposition of the oxide on a quartz or silicate surface.

One reason for conducting the above rudimentary tests was due to previous attempts at using the on-line AFS to measure elemental mercury in gases containing oxygen. It was found that the voltage signal from the AFS rapidly decayed, presumably due to the deposition of mercuric oxide on the quartz cell walls. The photosensitized formation of ozone can interfere with the ultraviolet measurement of elemental mercury by several ways: absorption of ultraviolet radiation by ozone; decrease in the population of mercury atoms by formation of mercuric oxide; and attenuation in the detected intensity of absorbed (AAS) or emitted (AFS) 253.7 nm radiation by elemental mercury due to the deposition of mercuric oxide on the quartz cell walls. Additionally, a reduction of the population of excited mercury atoms via energy transfer to oxygen (quenching) can influence the ultraviolet measurement of elemental mercury. However, the formation and deposition of mercuric oxide can be inhibited by heating the quartz photocell, although heating will neither stop the quenching of excited mercury atoms nor the absorption of 253.7 nm radiation by ozone. It is noted that several prototype continuous emissions monitors for mercury in flue gas, based upon absorption

of 253.7 nm light, use quartz cells that are heated to over 500°C.[8]

The direct irradiation of flue gas by 253.7 nm light could be a method for the removal of elemental mercury. A typical flue gas composition from a coal-fired utility can contain the following: 4% O_2, 16% CO_2, 6% H_2O, 1000 ppm SO_2, 500 ppm NO_x, 10 ppm hydrocarbons, 1 ppb Hg, and the remainder N_2. The concentration weighted quenching effect for each gas can be obtained from the cross-sectional area for quenching given by Bamford and Tipper[5]. Oxygen will be an important quenching agent in flue gas, but carbon dioxide, nitrogen, and water are also significant quenching species. The quenching of excited mercury atoms by carbon dioxide, nitrogen, and water could significantly reduce the amount of ozone formed by reactions (5) and (6) by reducing the population of excited oxygen molecules. Any ozone, a powerful oxidizer, formed through reactions (5) and (6) may also oxidize other components of the flue gas, such as sulfur dioxide, nitric oxide, carbon monoxide, and unburned hydrocarbons. These oxidations will compete with the oxidation of mercury by ozone shown by reaction (2). It is also noted that these oxidizable species are present in flue gas at concentrations which are orders of magnitude greater than the concentration of mercury. These factors could adversely impact the removal of mercury as mercuric oxide from flue gas by direct 253.7 nm irradiation.

Conclusions

Based on the experimental results presented in this research note and the experience of past

researchers, certain concerns must be addressed in the development of on-line ultraviolet continuous emissions monitors for the measurement of mercury in flue gas. The formation of mercuric oxide can interfere with the on-line continuous monitoring of elemental mercury in oxygen-containing gas streams. As other researchers have speculated, ozone formation can impact results since ozone can also absorb 253.7 nm radiation and can interfere with the determination of mercury even in the absence of reaction to form mercuric oxide. The quartz cells used in the ultraviolet detection of mercury could be heated above 500°C, the thermal decomposition temperature of HgO, in order to prevent the formation of mercuric oxide.

The relationship between the mercuric oxide and ozone formation through 253.7 nm irradiation warrents further attention as a technique to remove mercury from flue gas. Additionally, the presence of mercury and ozone in the upper levels of the atmosphere may have an environmental impact. Before being converted to mercuric oxide, as suggested by some researchers, elemental mercury could act as a photosensitizer for the formation of ozone in the upper atmosphere. Halogens in the upper atmosphere are known photosensitizers for the decomposition of ozone. Elemental mercury in the upper levels of the atmosphere may help mitigate some of the damaging effects of halogens upon the ozone layer. However, elemental mercury in the lower levels of the atmosphere may contribute to smog formation by acting as a photosensitizer for the formation of ground level ozone.

Acknowledgement

Evan Granite appreciates the support of a postdoctoral fellowship at the United States Department of Energy administered by Oak Ridge Institute For Science and Education. Robert Thompson of Parsons Infrastructure and Donald Martello of the United States Department of Energy provided outstanding chemical analyses.

Disclaimer

Reference in this paper to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement by the United States Department of Energy.

Literature Cited

(1) Greenwood, N.N. and Earnshaw, A., *Chemistry of the Elements*, Pergamon Press: New York, 1984.

(2) Dickinson, R.G. and Sherrill, M.S., Formation of Ozone By Optically Excited Mercury Vapor, in *Proceedings National Academy Science* **1926**, 12, 175.

(3) Volman, D.H., Photochemical Gas Phase Reactions in the Hydrogen-Oxygen System, pp. 43-82, in *Advances in Photochemistry*, vol.1, John Wiley: New York, 1963.

(4) Kondrat'ev, V.N., *Chemical Kinetics of Gas Reactions*, Pergamon: New York, 1964.

(5) Bamford, C.H. and Tipper, C.F.H., editors, *Comprehensive Chemical Kinetics*, volume 3, The Formation and Decay of Excited Species, Elsevier: New York, 1969.

(6) Maron, S.H. and Lando, J.B., *Fundamentals of Physical Chemistry*, Macmillan: New York, 1974.

(7) Horvath, M., Bilitzky, L., and Huttner, J., *Ozone*, Elsevier: New York, 1985.

(8) Silverberg, P., Cooper, C., and Ondrey, G., Monitoring Emissions Of Toxic Metals, Chemical Engineering **1999**, 106 (4), 43.

(9) Christian,G.D. and O'Reilly, J.E., *Instrumental Analysis*, Allyn and Bacon: Boston, 1986.

(10) Willard, H.H., Merritt, L.L., Dean, J.A., and Settle, F.A., *Instrumental Methods of Analysis*, Van Nostrand: New York, 1981.

(11) Moore, W.J., *Physical Chemistry*, Prentice Hall: New Jersey, 1972.

(12) Loeb, L.B., *Electrical Coronas*, University of California Press: Los Angeles, 1965.

(13) Murphy, J.S. and Orr, J.R., editors, *Ozone Chemistry and Technology*, Franklin Institute Press: Philadelphia, 1975.

(14) Biswas, P. and Wu, C.Y., Control of Toxic Metal Emissions From Combustors Using

Sorbents: A Review, *Journal of the Air & Waste Management Association* **1998**, 48, 113.

(15) Biswas, P., Wu, C.Y, Lee, T-G, Tyree, G., and Arar, E., Capture of Mercury in Combustion Systems by In Situ Generated Titania Particles with UV Irradiation, *Environmental Engineering Science* **1998**, 15 (2), 137.

(16) Perry, R.H. and Green, D., editors, *Perry's Chemical Engineers' Handbook*, 6th edition, McGraw Hill: New York, 1984.

(17) Roberts, L.M. and Walker, A.B., Electrostatic Precipitation, in *Kirk-Othmer Encyclopedia of Chemical Technology*, vol.8, John Wiley: New York, 1965.

(18) Murphy, D.M., The Composition of Aerosol Particles at 5-19 km Altitude. Annual Meeting of American Geophysical Union, San Francisco, CA, December 6-10, 1998.

(19) Murphy, D.M., Thomson, D.S., and Mahoney, M.J., In Situ Measurements of Organics, Meteoritic Material, Mercury, and Other Elements in Aerosols at 5-19 Kilometers, *Science* **1998**, 282, 1664.

(20) Schroeder, B., Springtime Transformation of Atmospheric Mercury Vapor in the Artic. Annual Meeting of American Geophysical Union, San Francisco, CA, December 6-10, 1998.

(21) Anlauf, K.G., Artic Ozone Measurements. Annual Meeting of American Geophysical Union, San Francisco, CA, December 6-10, 1998.

(22) National Air Quality And Emissions Trends Report 1997, EPA 454/R-98-016, United States Environmental Protection Agency, Office of Air Quality, Research Triangle Park, NC, 1998.

(23) Brooks Rand, Manual for CVAFS-2 Atomic Fluorescence Spectrophotometer, Seattle, WA, 1993.

Table 1. Photochemical Removal of Mercury as Mercuric Oxide

Test	**Carrier Gas**	**Time On-line (hr)**	**% Hg Removal**
Empty Cuvette Reactor	4% O_2 in N_2	28	83
Empty Cuvette Reactor	Air	6	100
Empty Cylindrical Reactor	Air	21.3	100
Packed Bed Sorbent	Air	6	42

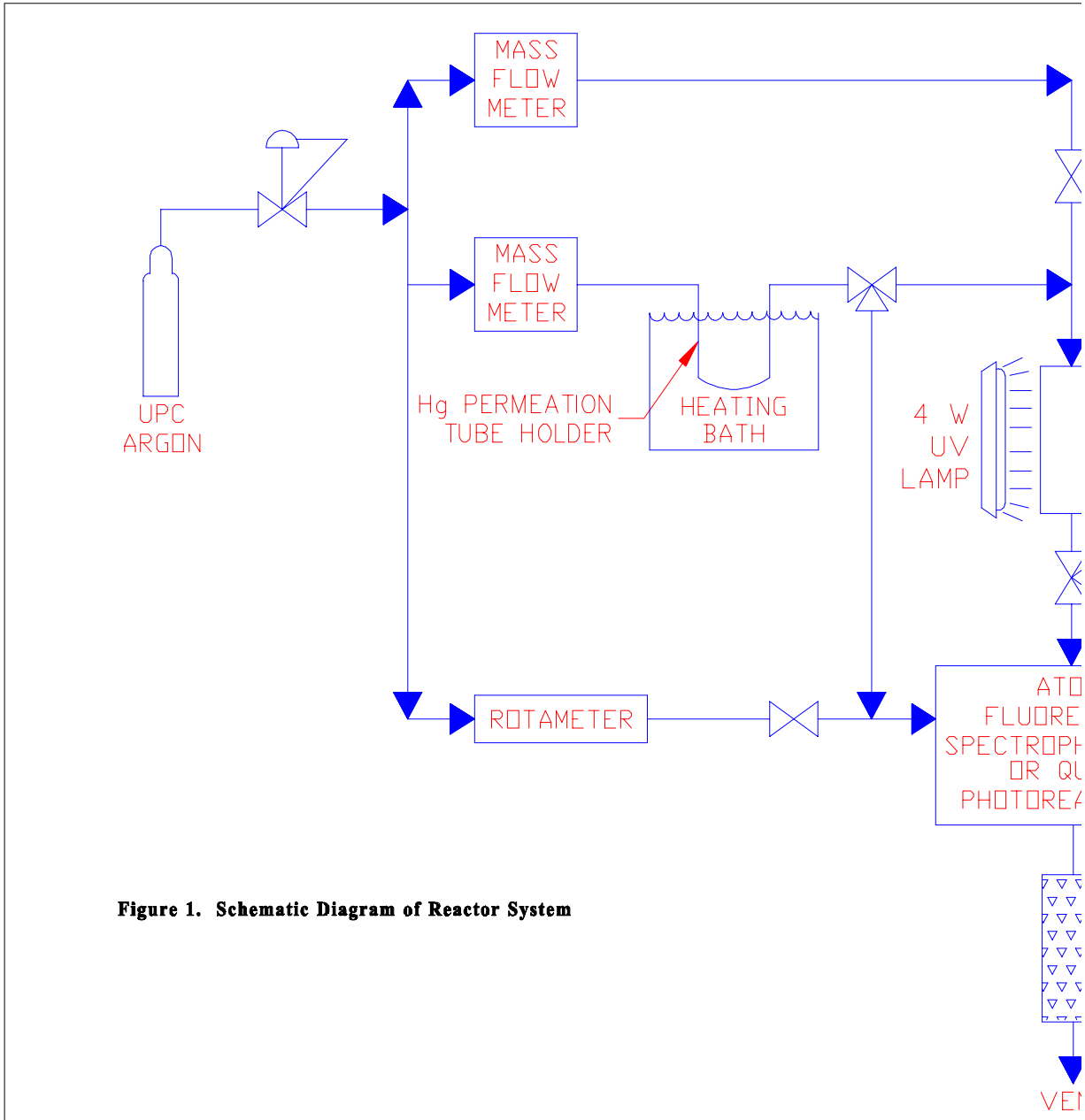

Figure 1. Schematic Diagram of Reactor System